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# OXIDATION AND REDUCTION MONITOR AND CONTROL SYSTEM

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## FINAL REPORT

by

J. B. Lantz and J. D. Powell

August, 1977

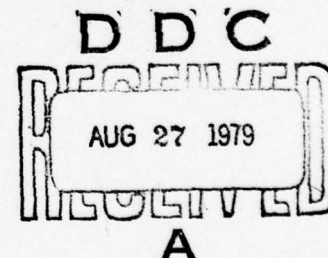
Prepared Under Contract DAMD17-76-C-6063

by

*Life Systems, Inc.*  
Cleveland, Ohio 44122

for

CIVIL ENGINEERING LABORATORY  
NAVAL CONSTRUCTION BATTALION CENTER  
Port Hueneme, CA 93043



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12/27p. Sulfide precipitation has been proposed as a heavy metal removal process for U.S. Navy drydock wastewaters. Development of this process requires an automatic system to control and monitor wastewater pH and sulfide levels during precipitation and hydrogen peroxide levels during subsequent oxidative sulfide removal. Reduction Monitor and Control System incorporates		

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the following features:

1. Control flexibility; nonlinear pH control capability, dual sensors, calibration loop, automatic or manual reagent flow control and dual acid/base control. Adaptable to alternate metals removal process.
2. Control precision; narrow, symmetrical control bands (e.g., typical pH control bandwidth of less than  $\pm 0.1$  pH, with very good averaging within this band).
3. Reagent Flow Control; wide speed range reagent control actuators; servo-tachometer generator metering pump systems.
4. Controlled reagent flow monitoring; monitoring of reagent pumping rate via calibratable meters on the instrumentation panel.
5. Ease of operation; all system controls, set points and monitoring recorders mounted on front instrumentation panel; illuminated pushbutton switches.

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This contractor's report presents detailed design information for a process control system for monitoring and controlling a heavy metal sulfide precipitation process. Experimental data and interpretation are presented on test and evaluation of this system.

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OXIDATION AND REDUCTION MONITOR AND  
CONTROL SYSTEM

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# FOREWORD

This report summarizes the concepts, characteristics, operation and checkout testing of an Oxidation and Reduction Monitor and Control (OARMAC) System for control and monitoring of a heavy metals removal process for wastewater. This system was developed and tested by Life Systems, Inc. during the period February through August, 1977 under U.S. Army Contract DAMD17-76-C-6063.

The Manager for Life Systems' Water Research and Development Programs is Gary G. See. The Project Manager for the OARMAC System development was Joel B. Lantz. Technical support was provided by the following:

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D. Johnson	Instrumentation package assembly and testing
D. Jones	Documentation
J. Lantz, PhD	System concept, reactor/sensor assembly design, instrumentation panel design and checkout testing
D. Powell	All system electronics design
J. Powell, III	Circuit card assembly
M. Prokopcak	Engineering drawings
N. Sasso	Circuit card assembly and testing
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The program's Technical Monitor was R. D. Saam, Civil Engineering Laboratories, Naval Construction Battalion Center, Port Hueneme, CA 93043.

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## SUMMARY

Sulfide precipitation has been proposed as a heavy metal removal process for U. S. Navy drydock wastewaters. Development of this process requires an automatic system to control and monitor wastewater pH and sulfide levels during precipitation and hydrogen peroxide levels during subsequent oxidative sulfide removal. Life Systems, Inc. has developed such a control system, called the Oxidation and Reduction Monitor and Control System. It incorporates the following features:

- Control flexibility: nonlinear pH control capability, dual sulfide sensors, calibration loop, automatic or manual reagent flow control and dual acid/base control. Adaptable to alternate metals removal processes.
- Control precision: narrow, symmetrical control bands (e.g., typical pH control bandwidth of less than  $\pm 0.1$  pH, with very good averaging within this band).
- Reagent Flow Control: wide speed range reagent control actuators; servo-tachometer generator metering pump systems.
- Controlled reagent flow monitoring: monitoring of reagent pumping rate via calibratable meters on the instrumentation panel.
- Ease of operation: all system controls, set points and monitoring recorders mounted on front instrumentation panel; illuminated push-button switches.

## INTRODUCTION

The U. S. Navy maintains sixty drydocks where hull cleaning and painting operations discharge heavy metals into facility wastewaters. When concentrations of the metals exceed levels permitted by the Environmental Protection Agency (EPA), reduction of these impurities is required prior to discharge.

Precipitation of the heavy metals as insoluble sulfides has been proposed as a particularly suitable method for treating these effluents which contain variable proportions of seawater. This process requires the addition of soluble sulfide at a controlled pH, removal of the precipitated heavy-metal sulfides, and subsequent removal of the excess soluble sulfide via oxidation. Experimental investigation of the controlled pH, sulfide and oxidant levels needed for treating effluents of variable composition required prior development of an automatic control and monitor system. This system had to control the addition of reagents to the wastewater stream to maintain specified concentrations and provide continuous monitoring of these concentrations.

Life Systems, Inc. (LSI) has designed, fabricated and checkout-tested such a system, the Oxidation and Reduction Monitor and Control (OARMAC) System for the Civil Engineering Laboratory (CEL) of the Naval Construction Battalion Center, Port Hueneme, CA. Application of the OARMAC to the sulfide heavy metals removal process is illustrated in Figure 1.

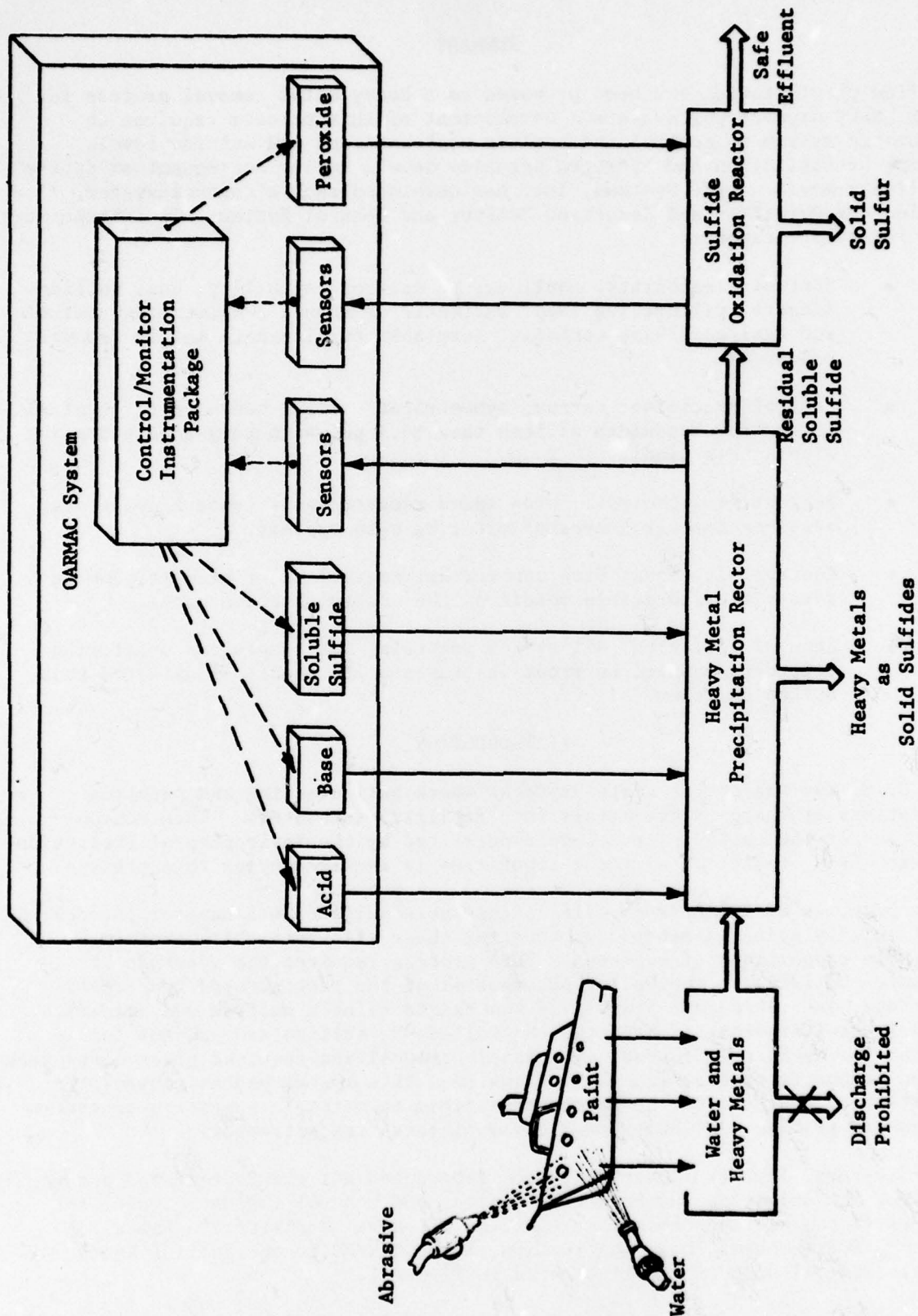


FIGURE 1 APPLICATION OF OARMAC TO SULFIDE METALS-REMOVAL PROCESS

The concepts, characteristics, operation and checkout testing of the OARMAC are the subject of this report.

#### OBJECTIVES

The general program objective was to develop a system for the automatic maintenance and monitoring of specified pH, soluble sulfide and peroxide levels in waste streams. Considerable flexibility in the design of the system was required because of its application as a process development tool under variable operating conditions and reagent consumption requirements.

During process development, selected pH levels between 5 and 7 and selected total soluble sulfide residuals between 1 and 100 mg/l must be simultaneously controlled in a stream of simulated wastewater. Controlled injection of acid or base and sulfide, plus precipitation of heavy metals, must be effected as the stream flows at 0.1 gal/min (379 cm<sup>3</sup>/min) through a well-stirred reactor of 0.5 gal (1893 cm<sup>3</sup>) capacity. Hydrogen peroxide must be subsequently added downstream such that selected peroxide residuals between 1 and 10 mg/l can be controlled in the system effluent during oxidation of residual soluble sulfides. Sulfide, pH and peroxide must be continuously monitored.

Specific objectives for system development were as follows:

- An automatic Control/Monitor Instrumentation (C/M I) Package, with suitable chart recorders for monitoring pH, sulfide and peroxide levels.
- Modification of the basic reactors, as furnished by CEL, for measurement of control parameters via suitable sensors (to be selected by agreement between LSI and CEL).
- Capability to monitor and control sulfide with either of two sensors.
- Provision in the modified precipitation reactor for calibrating sulfide and pH sensors without removal.
- Suitable actuators for feedback-controlled injection of reagents into the reactors, controllable by the Instrumentation Package.
- Choice of sulfide reagent for control applicability, handling safety and freedom from suspended matter.
- Reagent reservoirs of capacity for at least 8 hours run time.
- Safety considerations in design of sulfide and peroxide handling systems.
- System checkout testing to demonstrate proper functioning.



## SYSTEM CONCEPTS AND CHARACTERISTICS

The OARMAC System was designed to meet or surpass program objectives. Considerable flexibility was incorporated to enable use under a very wide set of operating conditions.

### Operational Description

The OARMAC system is described schematically in Figure 2. Influent is pumped into the precipitation reactor by means of a variable speed peristaltic feed pump, P5. A centrifugal pump, P4, stirs and circulates the reactor contents rapidly. Acid, base and sulfide reagents are added to the reactor contents upstream of pump P4, which mixes the solutions, and the resulting pH and sulfide levels are measured downstream with appropriate in-line sensors. Controller/Monitors, in combination with metering pumps P1, P2 and P3, perform the function of feedback control of reagent flow into this loop to maintain specified pH and sulfide signals at these sensors. The circulation rate is approximately sixty times the feed rate, aiding the attainment of favorable process control dynamics.

During process development at CEL, the effluent from the precipitation reactor will pass through a precipitate separator to remove insoluble sulfides prior to further processing.

Hydrogen peroxide is subsequently added to the process stream in the oxidation reactor to oxidize residual sulfides to elemental sulfur and sulfates. Residual peroxide levels are feedback controlled similarly to pH and sulfide levels in the precipitation reactor.

Needle valves V9, V11 and V13 facilitate sampling of influent and effluent. Check valves CV1 to CV5 (low cracking pressure types) are present on the reservoirs to safely equalize over-pressures or under-pressures, due to reagent decomposition and usage, with minimal contact of the reagents with the atmosphere. These reservoirs have sufficient capacity, 18.9 liters (5 gal), for approximately 12 hours of testing at maximum metering pump rates. Valves V5 and V7 can be closed to isolate pump P4 in the sensor manifold from the reaction system and enable circulation of calibration reagents over the sensors from an external reservoir through valves V4 and V6.

The complete OARMAC is pictured in Figure 3. The Reactor/Sensor Assembly is shown in Figure 4.

### Sensors

#### pH and Reference Sensors

The pH sensor is a standard industrial process-grade glass electrode. The reference sensors for both the precipitation and oxidation reactors are sealed-type silver/silver chloride electrodes, as supplied by CEL, with replaceable (and/or regenerable) ceramic frits to enable rejuvenation of the electrodes in the event of silver-sulfide junction clogging.

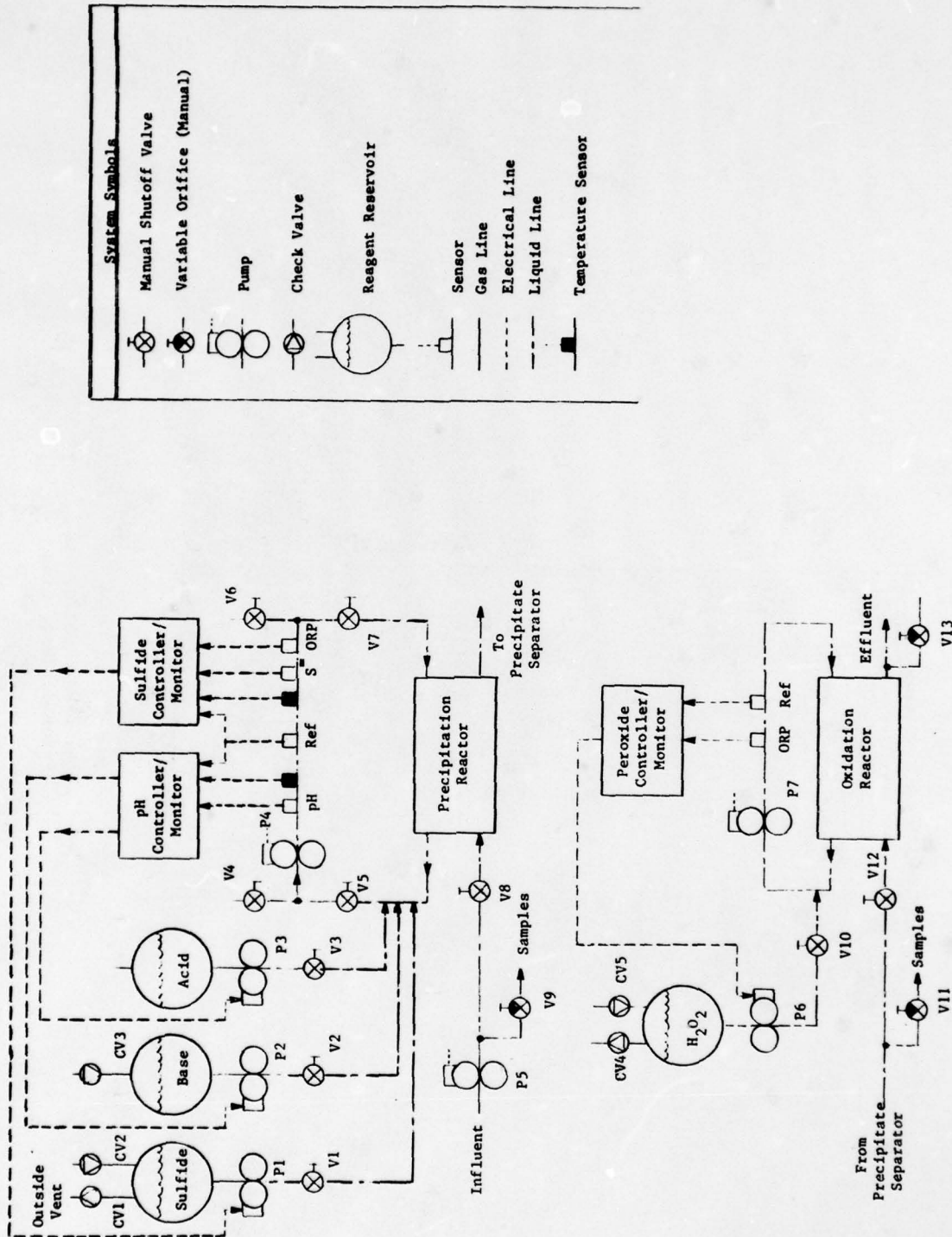


FIGURE 2 OARMAC SYSTEM SCHEMATIC



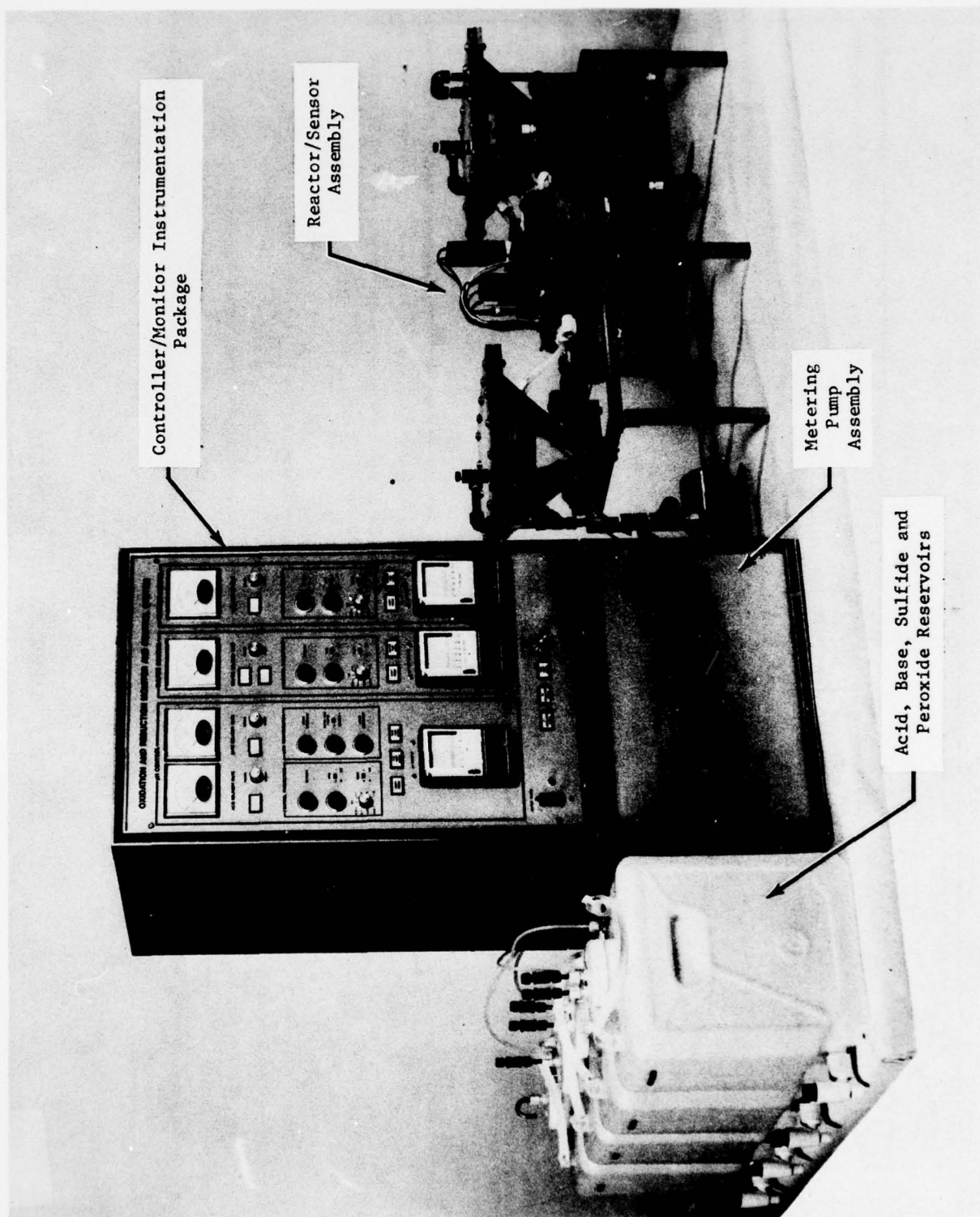


FIGURE 3 OARMAC FRONT VIEW

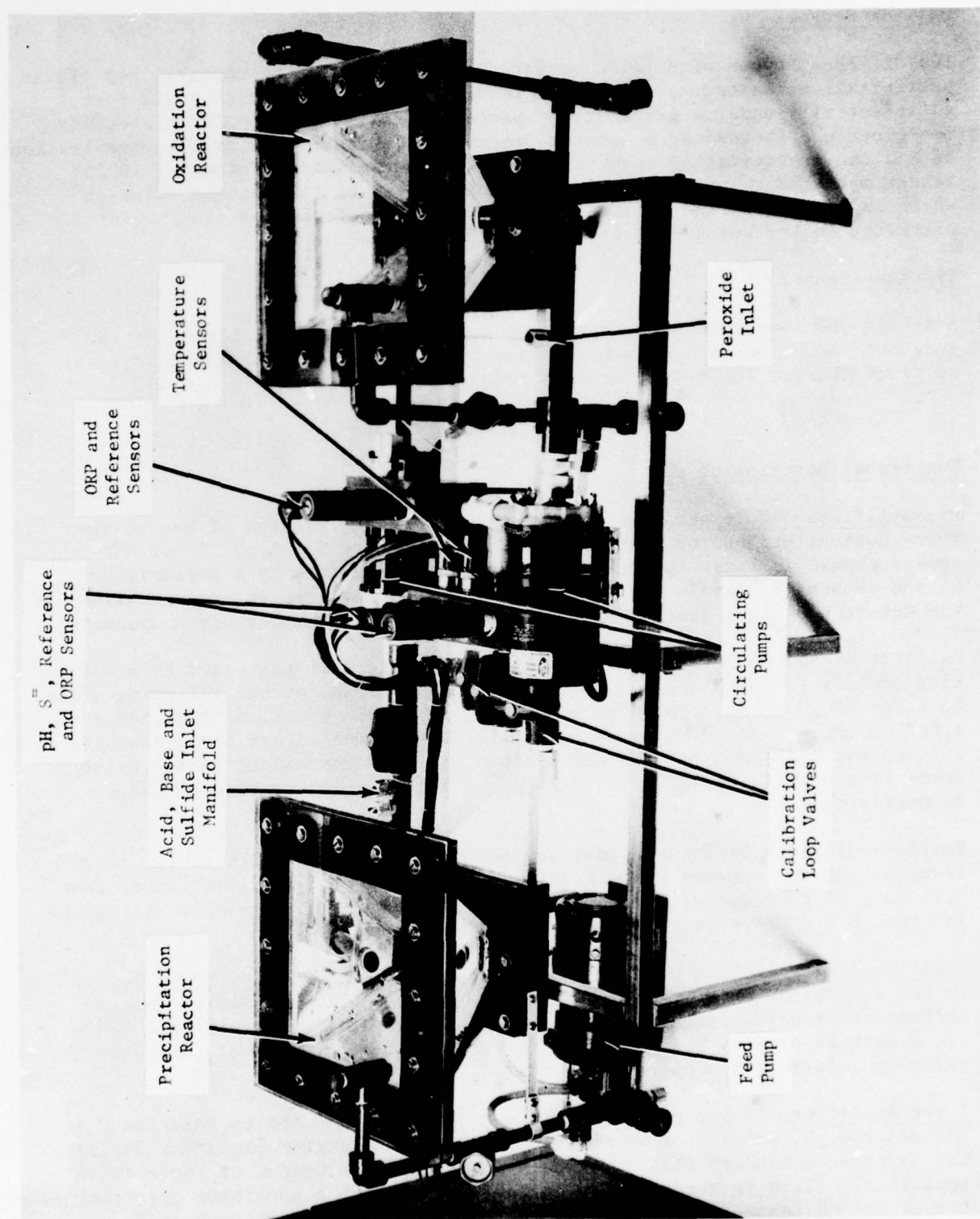


FIGURE 4 REACTOR/SENSOR ASSEMBLY

### Sulfide Sensors

Two different types of sulfide sensors are included in the control loop of the precipitation reactor to permit CEL to select the sensor which works most satisfactorily under a given set of process conditions. A sulfide specific ion electrode (hereafter  $S^-$  sensor) measures the relatively small concentration of  $S^-$ , the precipitating species. An Oxidation Reduction Potential (ORP) sensor measures relative oxidizing/reducing power of the process solution which is related to the sulfide content. Each electrode has its own input circuitry in the sulfide Controller/Monitor channel.

### Peroxide Sensor

A second ORP sensor is used to control peroxide addition in the oxidation reactor. Addition of hydrogen peroxide to the solution containing residual sulfides changes its character from reducing to oxidizing.

## The Controller/Monitors

### Functional Description

Preamplifiers and Temperature Compensators. A block diagram of one of the three Controller/Monitor channels is shown in Figure 5. A pH,  $S^-$  or ORP sensor signal is first converted to a low impedance form by a preamplifier.  $S^-$  and pH sensor signals are further compensated for temperature variations of the Nernst potential slope. The ORP signals are not temperature compensated.

Calibration and Buffer Amplifiers. This signal is next processed by a calibration amplifier, which may be set to output 5 V for any of the following spans: 2, 5, or 10 pH units, approximately 4, 10, or 20  $pS^-$  units, or 200, 500 or 1,000 mV ORP. A calibration potentiometer adjustment allows for sensor standardization and adjustment of the lowest span limit to correspond to any sensor level from 0 to 12 pH units, 0 to 24  $pS^-$  units, or -700 to +700 mV ORP, respectively.

Buffer amplifiers feed the signal in low output impedance form to the chart recorder and the control circuit while providing a variable gain factor from 0.75 to 1.25 to compensate for nonideal  $S^-$  sensor detection slopes (the gains for the pH and ORP channels should normally be set to 1.00).

Chart Recorders. Three Rustrak model 288 chart recorders monitor pH and  $pS^-$  in the precipitation reactor and percent ORP span in the oxidation reactor. Because these units, in effect, plot data at a rapid rate rather than trace it, a pattern of dots is recorded. The distribution density of dots provides valuable information about control stability.

Error Amplifier. A set point reference voltage is adjusted to correspond to the desired pH, sulfide or mV ORP control point. An error amplifier amplifies the difference between this reference voltage and the output of the buffer-amplifier. (This is accomplished in conjunction with a nonlinear gain compensator in the pH Controller/Monitor channel - see pH control discussion.)



**Gain Attenuator.** An adjustable gain attenuator provides a wide range of controller gains for optimization of control resolution and stability.

**Proportional Control.** In straight proportional control the output of the gain attenuator can be used to linearly vary the flow of reagents into the reactor. That is, a deviation of the amplified sensor signal from the set point varies the speed of the metering pump proportionately, when connected through the auto pump interface, the pump mode selector and the pump speed controller.

**Proportional-Integral Control.** In the OARMAC, however, more suitable control is provided by means of a reset amplifier, or integrator, in conjunction with the gain attenuator. The output of this device increases or decreases until the signal from the error amplifier is nulled. It then remains at a constant level and reagents are pumped at a constant rate until the error signal is again non-zero. Reagents will therefore be pumped at the rate necessary to maintain the sensor signal at the set point.

When the time constant of the integrator is short (reset rate is high) essentially straight proportional control is obtained.

**pH Control.** For optimum control of a process, the total loop gain (the total system response relative to a given deviation between sensor and set point signals) should remain approximately constant, regardless of the absolute signal level of the sensor. During pH control, however, the process gain portion of loop gain does not remain constant. That is, the pH change per increment of acid or base pumped into the process solution varies with its absolute pH level. Compensation of the electronic controller gain versus process solution pH is therefore necessary to keep the total loop gain approximately constant.

A process gain versus pH relationship can usually be approximated by a two or three section, two slope curve, equivalent to the titration curve for the given process solution. Where little acid or base is required to produce a given pH change (typically the mid-section of a titration curve) the change in reagent flow rate per change in sensor signal, the controller gain, should be reduced. This adjustment is accomplished automatically in the OARMAC via a nonlinear gain compensator, which provides reduced controller gain in the intermediate pH, or notch, region and full gain elsewhere. The notch gain reduction factor is variable between 0 and 100%. The lower and upper break points defining the notch are variable over the entire pH region.

The pH Controller/Monitor channel is designed to add either acid or base, depending on whether the process solution pH is above or below the set point. A deadband circuit has been included to provide a narrow pH region where neither acid nor base are added in an effort to avoid interactive acid-base addition.

(1) Shinskey, F. G., "pH and pIon Control in Process and Waste Streams," John Wiley & Sons, NY, 1973.

**Control Flexibility.** The circuits, actuators and sensors are adaptable to controlling and monitoring alternate or modified heavy metal removal processes. Other types of sensors may also be used after addition of relatively simple signal conditioning circuit cards at the controller inputs.

#### Circuit Layout

The buffer, error and reset amplifiers, the nonlinear gain compensator, the gain attenuator and the pump interfaces and mode selectors are wired on printed circuit cards. These cards are shown in Figure 5. Two identical cards are used for sulfide and peroxide control.

The temperature compensator for sulfide is wired on a separate card. The remaining circuits -- pH temperature compensator, preamplifiers, calibration amplifiers and pump speed controllers (modified commercial circuitry) -- are hardwired into the Instrumentation Package.

#### Spans

The pH and sulfide controller and recorder spans will normally be pH 4 to 9 and pS 6 to 16. Oxidation Reduction Potential spans should be adjusted to suit specific process requirements.

#### Metering Pumps

The peristaltic metering pumps are driven by motor/tachometer-generators, which permit close speed control and a much larger range of ratios (1 to 1,000) than typical (1 to 20). Manual adjustment and tachometer monitoring of the metering pump speed is also provided.

#### Instrumentation Panel

The instrumentation panel shown in Figure 7 incorporates all required controls for system operation: metering pump speed readouts (calibratable in terms of reagent delivery rate), automatic/manual reagent pumping rate selection, dual sulfide sensor selection, proportional-integral and nonlinear controller adjustments and chart recorders. Easily read, illuminated pushbutton switches are used for mode selection and component power initiation.

#### Interfaces

Figure 8 shows the electrical and fluid interfaces, the metering pumps and shutoff valves V1, V2, V3 and V10. Separate reference sensors may be used for each channel as indicated by the separate connectors provided on the back of the interface panel. In normal operation, however, a single reference electrode for the pH channel is used, and its output is jumpered to the S<sup>-</sup> sensor and sulfide ORP reference inputs behind the panel by means of a plug board.

The pumps and fluid interfaces are mounted in an inert tray to prevent possible corrosion of the assembly during tubing changes or accidental reagent leakage.



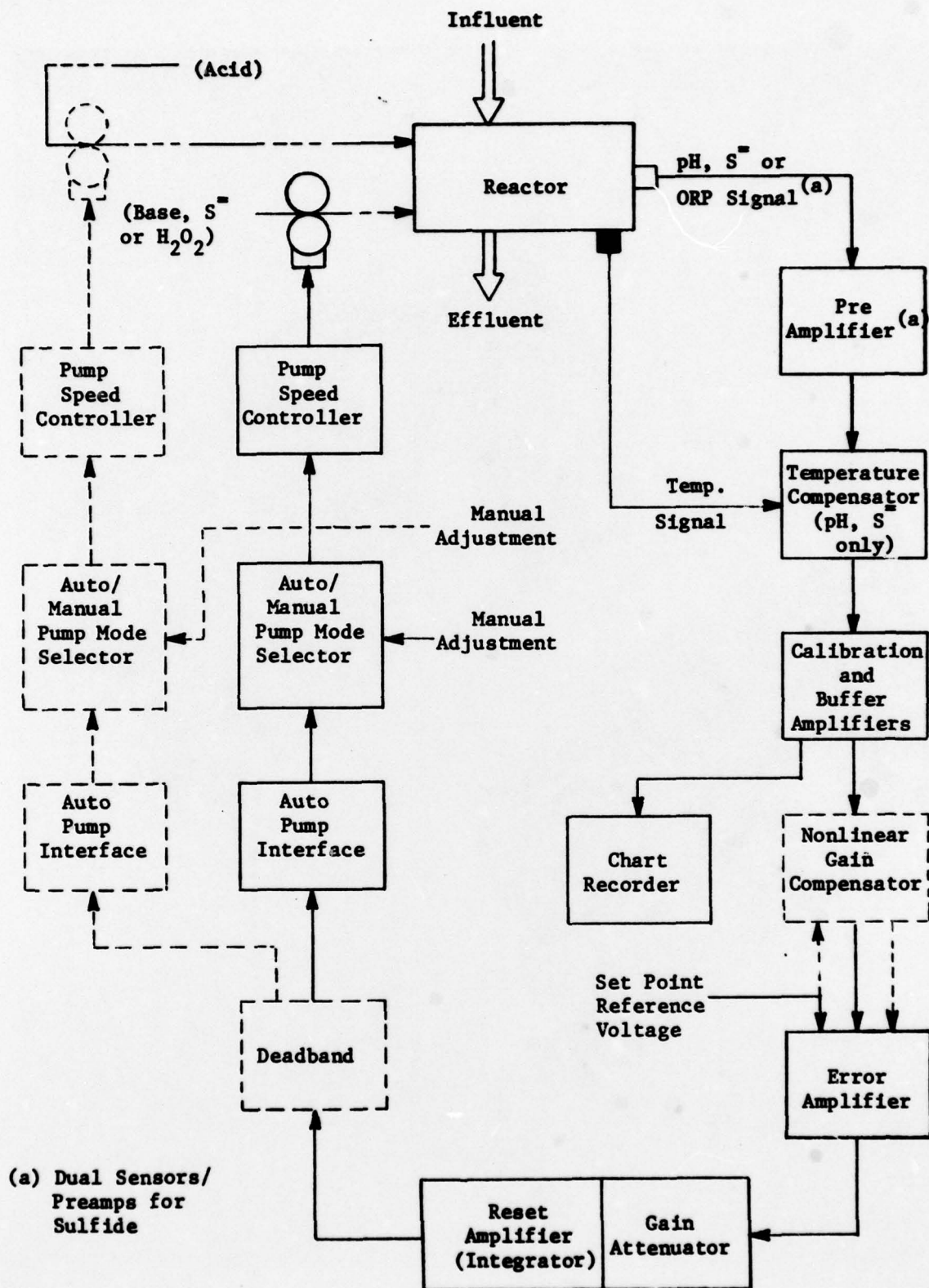


FIGURE 5 CONTROLLER/MONITOR BLOCK DIAGRAM (ONE CHANNEL)

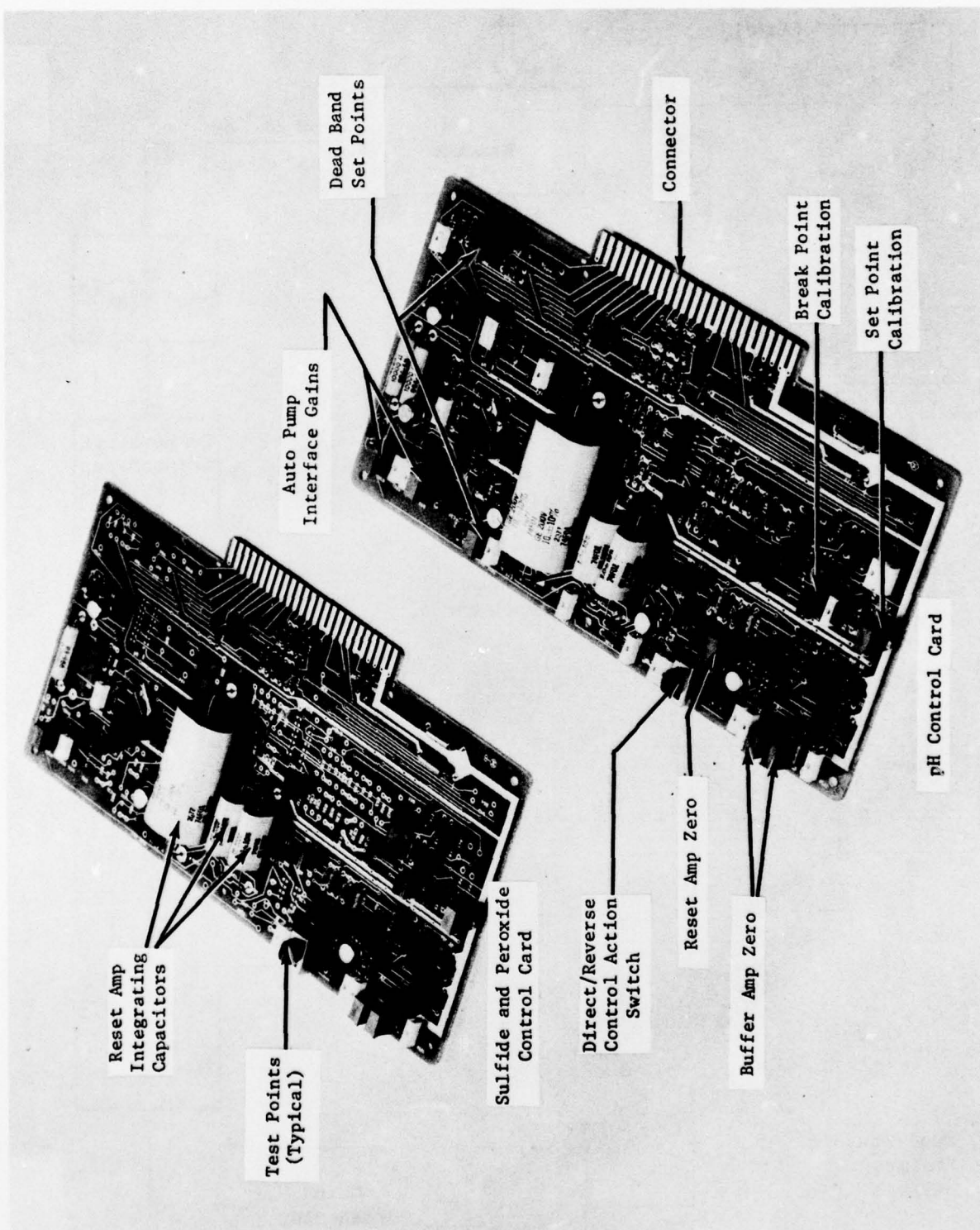


FIGURE 6 CONTROL FUNCTION PRINTED CIRCUIT CARDS

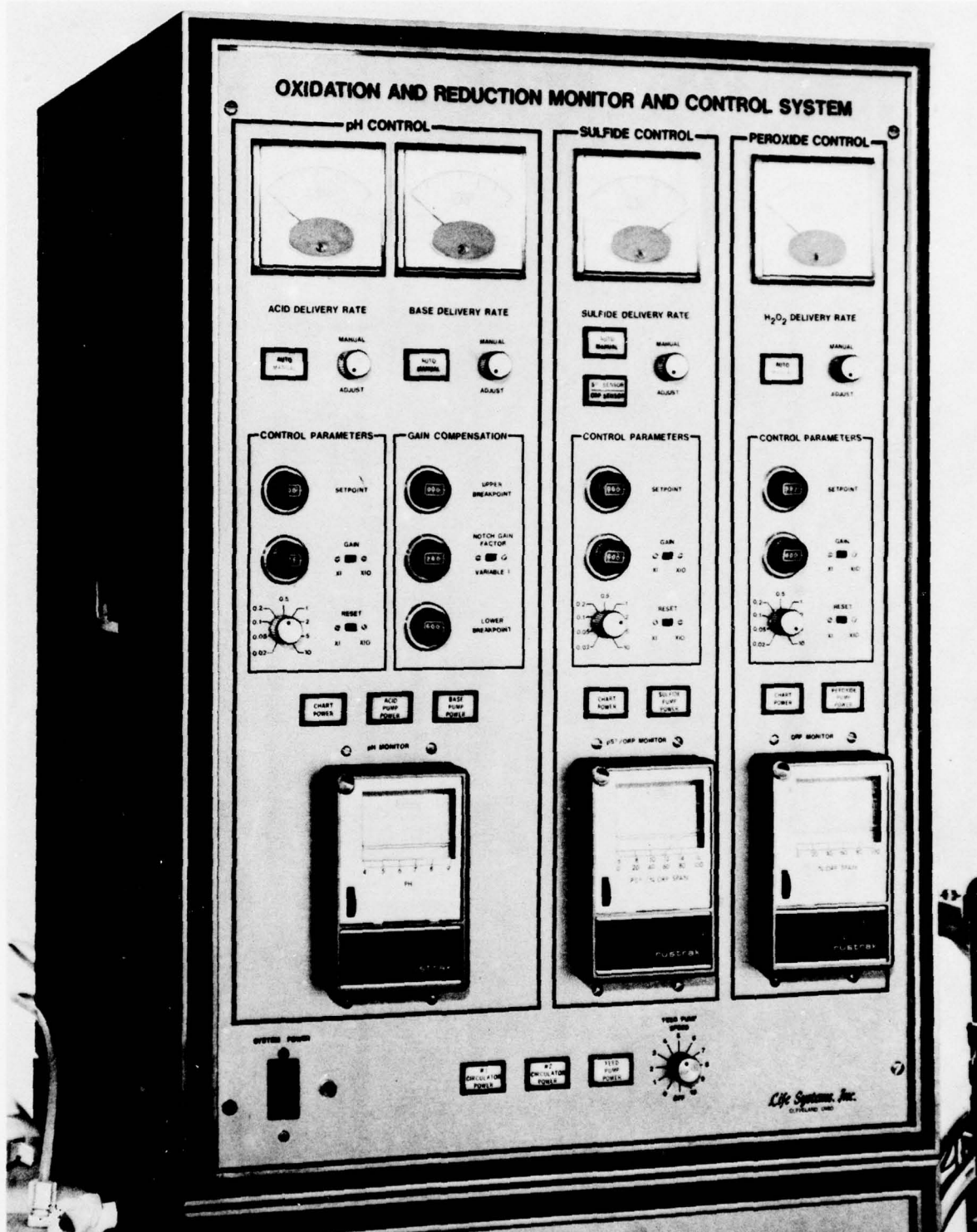


FIGURE 7 INSTRUMENTATION PANEL



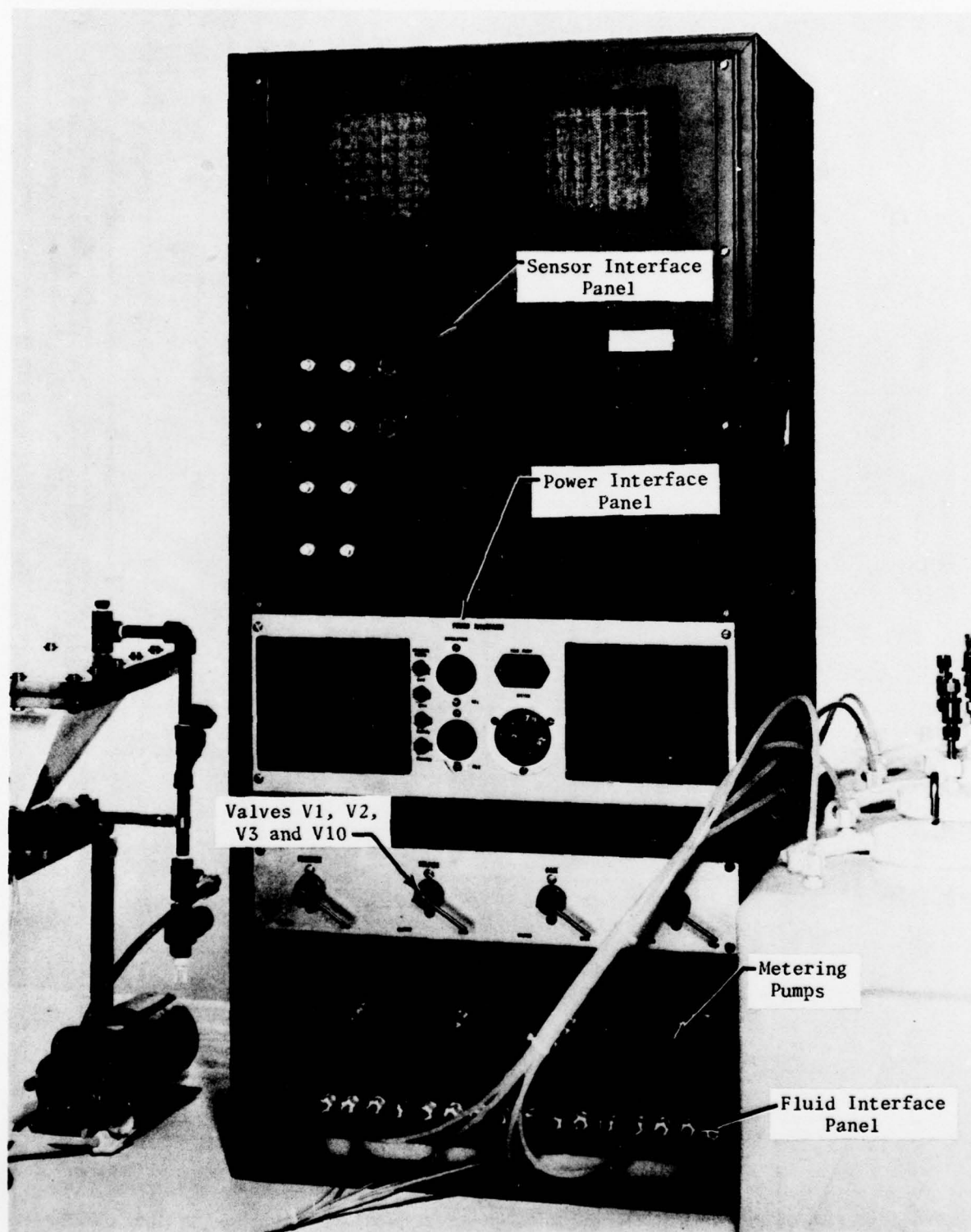


FIGURE 8 SYSTEM INTERFACES

### Interior Controls

Figure 9 shows the rear interior of the C/M I package, accessible by opening a door. The printed circuit cards, the sensor calibration potentiometers, an internal sensor signal monitor and pump speed calibration adjustments are located here. The preamplifiers are mounted directly behind the sensor interface panel in a separate metallic enclosure to maximize electrostatic shielding.

### CHECKOUT TESTING AND OPERATING PROCEDURES

The OARMAC system was operated under several control conditions with tapwater as an influent to check for proper functioning. The general operating methodology required for the OARMAC system, as exemplified by actual procedures used during testing, and the results of checkout tests will be discussed.

#### pH Control

##### Sensor Calibration

The sensor was calibrated by circulating pH 7 and pH 4 buffers through the sensor manifold of the precipitation reactor. This section of the reactor was first flushed with tapwater, isolated from the reactor, and drained. At least one liter portions of buffer solutions were circulated, such that the small amount of residual tapwater remaining in the calibration loop had a minimal effect on the pH. The No. 1 calibration potentiometer (see Figure 9) was adjusted such that the pH recorder indicated pH 7 for the corresponding buffer. The recorder indicated 3.8 during subsequent pH 4 buffer circulation.

##### Gain Compensator Settings

To determine the break points defining the pH notch region where controller gain should be reduced, and the notch gain factor, a titration curve should be obtained. Since the pH is controlled with strong acids and bases, the pH titration may be started at an arbitrary pH as long as the span of the Controller/Monitor (pH 4 to 9) is covered in the curve.

The titration curve is then approximated by two or three straight lines. The ratio of the smallest slope (or average of two smallest slopes) to the larger slope of these lines is the notch gain factor. The relative positions of the slope-change points in the approximated curve over the Controller/Monitor span range determine the upper and lower break point settings (expressed as percent of span).

Figure 10 is the titration curve determined for the tapwater used as the checkout-test influent. (A similar, though slightly displaced, curve was obtained for water containing 10 ppm sulfide.) There are two high slope regions over the pH 4 to pH 9 span. For control in the upper half of the pH span, the notch gain factor is the ratio of slopes 2 and 3.

$$\text{Notch Gain Factor} = \frac{2.28 \text{ cm}^3/\text{pH}}{7.15 \text{ cm}^3/\text{pH}} = 0.28$$



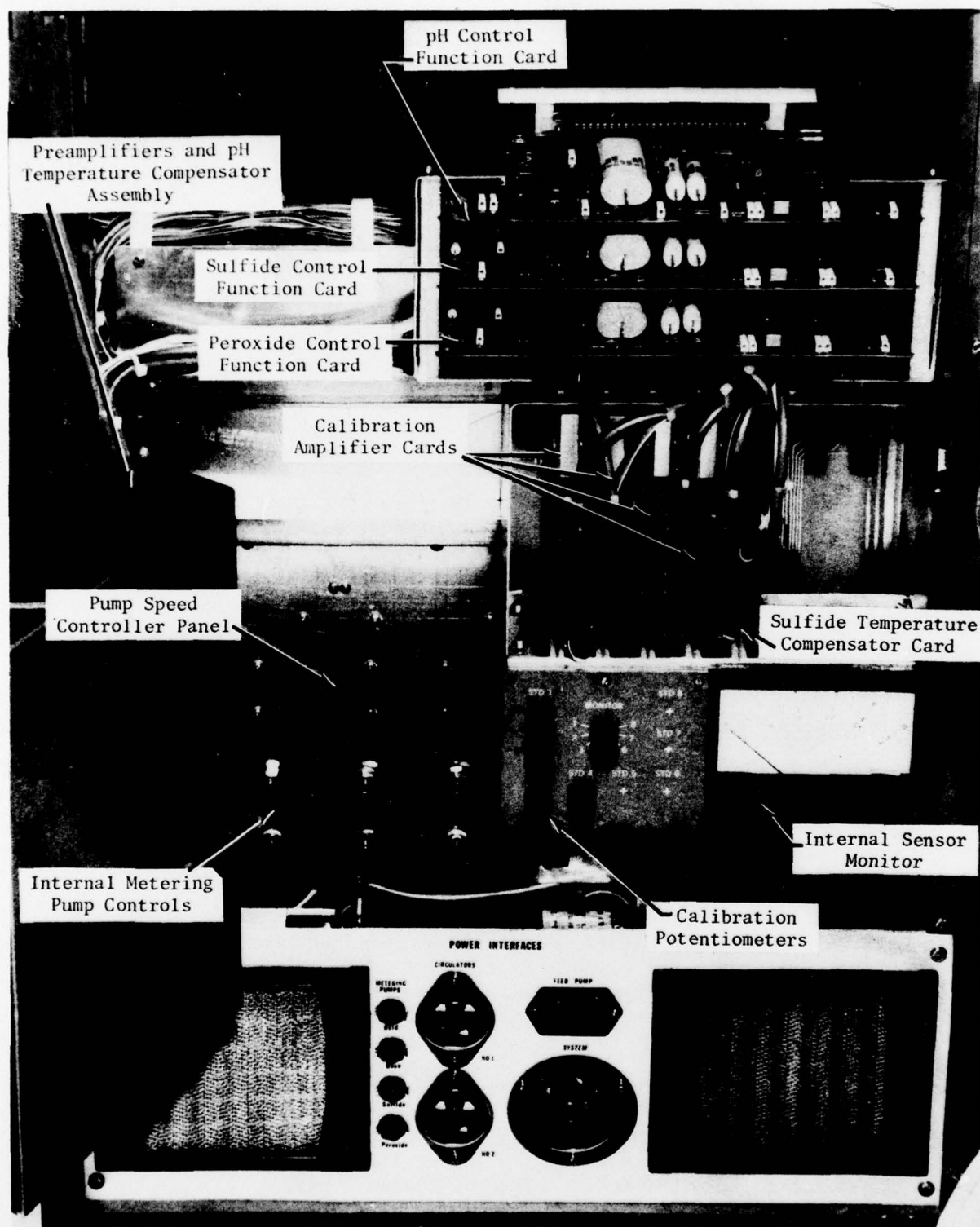


FIGURE 9 INTERIOR OF CONTROL/MONITOR INSTRUMENTATION PACKAGE

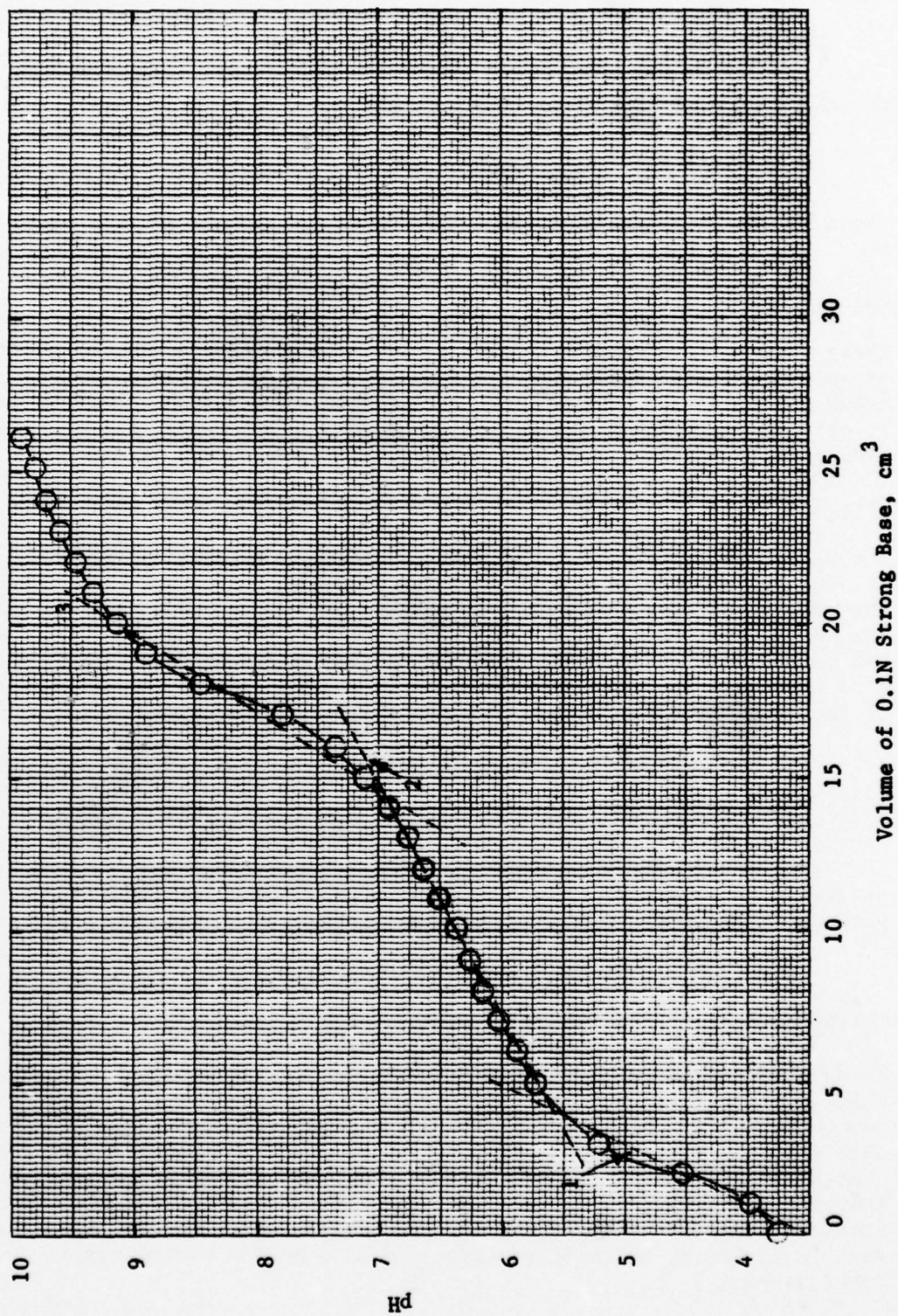


FIGURE 10 pH TITRATION CURVE FOR TAP WATER

The notch does not start until pH 7, corresponding to 60% of the controller span. That is,

$$\text{Lower break point} = \frac{\text{pH } 7 - \text{pH } 4}{\text{pH } 9 - \text{pH } 4} (100) = 60\%$$

The notch ends at pH 9 or at 100% of the controller span.

$$\text{Upper break point} = \frac{\text{pH } 9 - \text{pH } 4}{\text{pH } 9 - \text{pH } 4} (100) = 100\%$$

(Because of the relatively small differences in slopes in this case, these settings also sufficed for control at pH 5 during checkout testing.)

#### Gain and Reset Settings

These settings are generally made on a somewhat trial-and-error basis. With reset on (smallest time constant), maximum gain is increased until the system shows instability. Then reset is decreased until control stability within an acceptable range is obtained. Additional adjustments of gain and reset may be desirable to optimize control dynamics.

#### Checkout Tests and Results

The OARMAC was checked out for general control capabilities at pH 5, 6, 7 and 8, with 0.1 N sulfuric acid and sodium hydroxide solutions as control reagents. The results of these tests are summarized in the pH checkout column of Table 1. The pH control bands were narrow. Oscillations within these bands were rapid and uniform, such that pH variations in the precipitation reactor effluent were certainly much narrower than the bandwidth, due to the integrating effect of the reactor.

Acid/base control interaction was observed when both acid and base pumps were operated automatically. That is, both acid and base were pumped into the reactor simultaneously, with one reagent compensating for addition of the other. Despite the additional reagent demand due to this factor, reservoir capacity is sufficient for about 12 hours of testing. The controller deadband circuitry is scheduled to be modified to avoid this interaction. The scaled-up process will likely require only single reagent (acid or base) control, however.

#### Sulfide Control

##### Calibration of Sulfide Specific Sensor

To calibrate this sensor it is necessary to use a solution with a known total sulfide concentration and a selected pH so that the concentration of  $\text{S}^{2-}$  ion can be calculated from equilibrium relationships. It is also necessary for this solution to contain an antioxidant to avoid deterioration of the sulfide content due to air oxidation. For checkout testing, a pH and oxidation-stabilized solution of sulfide was prepared from the following: 98 mg sodium sulfide (sulfide source), 56 g boric acid (pH buffer source), 72 g ascorbic acid (antioxidant and buffer source), plus some 10% sodium hydroxide solution (pH adjustment).



The buffer and antioxidant were added to 4 liters of water and the pH was adjusted to 7.6 with sodium hydroxide prior to adding the sodium sulfide. The OARMAC calibration loop was isolated from the precipitation reactor and drained, the 4 liters of solution were circulated through the loop for a short period, and the sulfide (dissolved in a small amount of water) was added to this solution while circulating. Circulation was not continued any longer than necessary for mixing and calibration, to avoid aeration. The No. 2 calibration potentiometer (Figure 9) was then adjusted such that the sulfide recorder indicated  $pS^-$  8.7, the calculated approximate  $S^-$  level for this solution.

#### Gain and Reset Settings

Gain and reset settings were selected as for pH control.

#### Checkout Tests and Results

The sulfide channel was checked out for control at the set points of  $pS^-$  8.7 and 14.0 with 0.1 N sodium sulfhydryde (NaHS) as reagent. pH was simultaneously controlled. The combined effect was control of total sulfide.

The results of these tests are listed under sulfide checkout in Table 1. The control bands were relatively narrow and symmetrical. As for pH, variations in effluent sulfide concentrations are projected to be much smaller than control band precisions due to the averaging effect of the reactor. The recorded control points and bands are expressed both as  $pS^-$  and as total sulfide based on the analyzed effluent pH values.

Observations suggest that the reference electrodes may drift slowly due to silver sulfide formation on the junctions. If so, either frequent reconditioning of the junctions or replacement with alternate reference sensors (e.g., double junction types) will be advisable.

#### ORP Calibration

The sulfide channel was not calibrated in the ORP mode although functional capability of this channel was checked on the electronics bench. Specific process testing in this mode will be carried out by CEL under specific process development conditions.

### Peroxide Control

#### Calibration

The most sensitive Controller/Monitor span, 200 mV, was selected. The center scale of this range was adjusted to 0 mV with the No. 4 calibration potentiometer (0  $\pm$  100 mV effective span). The ORP was not calibrated with peroxide solutions, however.

#### Gain and Reset Setting

Gain and reset settings were selected as for pH and sulfide.

TABLE 1 CHECKOUT TEST RESULTS

	pH Checkout			Sulfide Checkout			Peroxide Checkout		
pH Control Data									
Set point pH	5.0	6.0	7.0	8.0	8.0	7.7	7.7	7.7	7.7
Monitored pH	4.9	6.1	7.1	8.1	8.1	7.7	7.8	7.8	7.8
Control Band, $\pm$ pH	0.05	0.08	0.14	0.05	0.05	0.06	0.06	0.06	0.06
Band Symmetry (a)	E	VG	VG	VG	VG	VG	VG	VG	VG
Analyzed pH	-	5.9	-	-	8.1	7.7	-	-	-
Gain Setting	20	20	20	20	20	20	20	20	20
Reset Setting	20	20	2	20	20	20	20	20	20
Sulfide Control Data									
Set point, pS=					8.7	8.7	9.0	9.0	9.0
Monitored Sulfide					8.9	8.8	9.2	9.2	9.2
As pS=					3.5	12.1	4.5	4.5	4.5
As Total S (mg/l)					0.10	0.15	0.10	0.10	0.10
Control Band					0.7	3.5	1.0	1.0	1.0
As $\pm$ pS=					E	VG	VG	VG	VG
As $\pm$ Total S (mg/l)					20	600	600	600	600
Band Symmetry (a)					20	20	20	20	20
Gain Setting									
Reset Setting									
Peroxide Control Data									
Set point, mV									
Monitored ORP, mV									
Control Band, $\pm$ mV									
Band Symmetry (a)									
Gain Setting									
Reset Setting									

(a) E = Excellent

VG = Very Good, occasional random points

G = Good, slight long term oscillation (few minutes period)

### Checkout Tests and Results

General control capability of the peroxide channel was checked at approximately 40, 60, 80 and 100 mV, with 0.1 M hydrogen peroxide as reagent. The pH and sulfide were controlled upstream. The control band was very narrow and symmetrical, as indicated in Table 1, (peroxide checkout column). The uniform offsets between set point and monitored mV levels were attributed to inexact centering of span midpoint. Based on the approximate average peroxide metering pump speed the peroxide residual controlled was estimated to be about 30 mg/l during control at 100 mV.

### CONCLUSIONS

An automatic control and monitor system has been successfully developed which surpasses application objectives:

- Checkout testing of this system beyond basic program requirements has demonstrated: narrow, symmetrical control bands (e.g., typical pH control bandwidth of less than  $\pm 0.1$  pH, with very good averaging within this band), favorable process dynamics and ease of operation. Observed acid/base interactions will not interfere with application requirements.
- The following features surpass design objectives:
  - Gain-compensated pH control
  - Extremely wide-range metering pumps
  - Monitoring and manual control of reagent injection
  - Flexibility that extends applications beyond currently planned reaction conditions
  - Attractive, integrated packaging of instrumentation

### RECOMMENDATIONS

1. Develop a compact, dedicated control and monitor system for heavy metal-removal pilot plant, and ultimately drydock plant, applications.
2. Develop a bench-scale process and the control and monitor system for recycling sulfide and recovery of heavy metals. Such a system would:
  - Minimize or eliminate sulfide reagent requirements and associated storage and handling
  - Provide for probable defrayment of wastewater processing costs and recycling of valuable natural resources via resale of recovered metals
  - Eliminate sulfide sludge disposal and its possible impact on the environment



Possibly eliminate or minimize the requirement for an oxidation process step to remove soluble sulfide residuals

The recycling control and monitor system would be designed for compatibility with the OARMAC System developed under the current program.

3. Develop techniques and/or systems to permit frequent automatic calibration of process sensors without disturbing the process, or develop sensor systems requiring infrequent calibration.
4. Develop a peroxide-specific sensor to improve control and monitoring of peroxide levels in an oxidation reactor.
5. Develop a sensor system to continuously indicate total sulfide at variable process pH.
6. Investigate alternate heavy metals removal processes (e.g., hydride reduction) at the bench-scale.
7. Solidify heavy metal treatment criteria and analyze experimental data to determine which of the competitive heavy metal treatment process, or combination of processes, best meet these criteria on a cost/effectiveness basis.